NUCLEAR SCIENCE AND TECHNIQUES 25, 030201 (2014)

Roadside dust contamination with toxic metals along industrial area in Islamabad, Pakistan

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(Received August 22, 2013; accepted in revised form October 11, 2013; published online June 20, 2014)

An investigation has been carried out to understand the contamination characteristics of roadside dust in the industrial area of Islamabad, Pakistan. The amounts of Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Pb, Zn, Ga, As, Se and Cd were determined from 95 roadside dust samples collected along the Islamabad industrial area using Proton Induced X-ray Emission (PIXE). The results indicated that concentrations of all elements, except Cd, in the roadside dust were significant. The results of the enrichment factor show that the elementary composition of the roadside dust could be categorized as soil elements from the crust of the earth and elements from anthropogenic pollution. The high enrichment factors imply that elements such Cr, Cu, Pb, Zn, As, Se, Cd, Ni, Co and S came from anthropogenic activities. The source of metal contamination was identified using multivariate statistical analysis. It has been concluded that Ca, Sc, Ti, V, Mn and Fe mainly originate from crustal sources; Cr, Cu, Ni, Pb, Zn and Ga are associated with point-sources from industrial pollution/traffic; and S, Cl, K, As and Se are mainly related to oil/coal combustion.

Keywords: PIXE, Roadside dust, Toxic metals

DOI: 10.13538/j.1001-8042/nst.25.030201

I. INTRODUCTION

Solid matter, comprising soil, metallic elements from anthropogenic activities and natural biogenic matter, is referred to as dust [1]. Soil is composed of inorganic matter, humus, living organisms, air, and water. Particle from vehicle exhaust, tire wear, weathered street surface, brake lining wear, and residues from oil lubrication, make up anthropogenic materials. Natural biogenic matter is vegetation crushed by moving vehicles [2–4]. Dust particles coming from the atmosphere and collecting along the sides of a road are called road-side dust [5, 6]. Displaced soil and atmospheric aerosols are the two main sources of roadside dust and heavy metals found in the dust [1].

Furthermore, vehicle emissions, construction industry activities, corrosion of metallic support systems, heating systems and sinking particulate matter, all contribute to roadside dust [3, 6]. This roadside dust will not remain deposited in place for long as it can easily be re-suspended into the atmosphere, and contributes significantly to trace elements. The dust may also get into dams or other water bodies in the form of dissolved solids after being washed away by rainfall in street run-off [1].

Consequently, the composition of roadside dust in urban areas is affected to a great extend by human activities. Both anthropogenic and natural biogenic materials which can be crushed by moving vehicles contribute directly to roadside dust [7]. Soil and roadside dust can supply particulate matter and pollutants to the hydrosphere and atmosphere during run-off, re-suspension, leaching, and weathering. Rapid industrialization and urbanization have resulted in almost half of the world population moving into urban areas where their

activities are increasing the amount of contaminants being discharged into the urban environment. Hence, various environmental problems have arisen, with pollution from toxic metals as a major issue, especially in urban soils and roadside dust [8, 9].

Metals are helpful indicators of environmental pollution as they are typical contaminants in urban environments. Heavy metals in the soil come from two main sources: (i) natural background, representing heavy metals obtained from parent rocks; and (ii) anthropogenic contamination, including farming and agriculture-related activities and sewage sludge. There are generally more heavy metals in soils from anthropogenic than from natural sources.

The condition of urban soils and heavy metal contamination in Pakistan has hitherto not been adequately addressed, and attempts to come up with extensive surveys using systematic sampling strategies have been limited. There is need to understand the changes in the characteristics of the soil and their spatial variation so as to combine traditionally based soil survey approaches and associated soil interpretations [10–12]. Focus along these lines in terms of the condition of the soil is limited. It is therefore critical to analyze the effects of land use on metal levels in soils in order to come up with legislation aimed at reducing metal inputs into the soils and preservation of soil functions.

Therefore, this study attempted to (1) determine average concentrations of Cu, Zn, Ni, Pb, Cr and Cd; (2) define the natural and/or anthropogenic sources of these metals using enrichment factor; (3) establish the local or exotic sources causing contamination in soils; and (4) expand the trace metal database for roadside dust in Islamabad. The results of this research may be useful for the municipality as there is lack of information regarding heavy metals in roadside dust in Islamabad and its relationship with environmental factors. This information may also be useful in alleviating metal contamination in pursuit of Islamabad's development as an international megapolitan.

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II. MATERIALS AND METHODS

A. Study area

The city of Islamabad is located near the Margallah Hills at the northern edge of the Potohar Plateau supporting natural terraces and meadows across the whole area. Streams flow down from Margallah Hills and ranges of the Murree Hills, and converge with a profusion of small streams like Soan and Kurang tributaries passing through the city. The growth of the urban area is taking place at a high pace leading to the deterioration of the vegetation of the area. Islamabad is situated at latitude 33.72°N and longitude 73.07°E, and at altitudes of 457-610 m (asl). The area is in a semi-arid region with mild summers and winters and with rugged topography varying in elevation, mainly comprising steep slopes and gullies. The natural soils of the area come from wind and water laid deposits, and sedimentary rocks. The soils from wind deposits vary from dark brown to yellowish brown in color and the subsoil is usually calcified or calcareous silt loam [13]. Because of recent accelerated urbanization and developmental activities, adverse effects of discharging untreated sewage wastes and dumping of solid waste on the soil have been observed [14].

B. Sampling

For this study, sector I-9, being the industrial areas of Islamabad, was selected to find the extent of contamination of toxic metals in roadside dust, which might affect the health of the inhabitants of these areas. A total of 95 sampling sites were selected from sector I-9. Because of the rapid changes in soil use in the urban area, the identified sites were not further divided into different categories. The dust samples were collected from both sides of the road using a spatula and a small brush, and then mixed thoroughly to obtain a representative sample for each site. All the collected samples were kept in sealed polyethylene (PE) bags to avoid contamination and thereafter the samples were taken to the laboratory for preservation.

C. Sample preparation

The dust samples were dried at room temperature and sieved using a 2-mm sieve to remove unwanted particles like stones and debris. The dried samples were then mixed thoroughly and about 1 g of the homogenized sample was grounded into powder. From each homogenized sample about 180 mg were pelletized, using a press and a 13 mm die, to obtain 1 mm thick pellets.

D. PIXE analysis

The pelletized samples were irradiated with 3.0 MeV proton beam from the 5 MV Pelletron Tandem accelerator installed at Experimental Physics Lab, National Centre for Physics, Islamabad. The calibration and standardization of the newly installed PIXE chamber for both thick (TiV/Fe alloy) and thin (SRM 2783) targets was carried out using NIST standard reference materials. The diameter of the collimated proton beam was 2 mm. A 100 µm thick Mylar, "funny" filter was used during the measurements and this reduced the count-rate to ensure a dead time of less than 10% at beam currents of 2–5 nA. Observation of the samples after irradiation showed no apparent damage. The emitted X-rays were detected using a 30 mm² Si(Li) detector with an energy resolution of 138 eV (FWHM) at 5.9 keV of Mn. The PIXE data was analyzed using the computer code GUPIXWIN.

III. RESULTS AND DISCUSSION

A. Total contents of metals

The concentration levels of the elements found in roadside dust in Islamabad are as shown in Fig. 1. The concentrations with respect to sampling locations for Zn and Cu are shown in Fig. 2. It is evident that the concentration of metals varies with distance from source.

The elements determined include Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se and Cd, and elemental levels in the dust samples were ranked as Fe >Ca >Co >Sc >K>Ti>Mn>Zn>Pb>Cu>Ni>Cr>V>Si>S>As >Ga >Cl >Se >Cd. The soil background values of Islamabad were used as references [15]. The mean concentration of measured heavy metals, except Cd, greatly exceeded the reference values. The levels of Cu, Ni, Pb and Zn were over 3 times greater than the reference values. Worldwide concentrations of these elements in road dust as found in literatures are given in Table 1. Comparatively, metal concentrations for different studies show different metal diversity and variable magnitude of concentration. In this study, the extent of pollution is significant for several metals at different sites based on the absolute metal content. Compared with metal contents in other cities such as Ottawa (Canada) (Table 1), the mean value of Cd, Cu, Ni, Pb and Zn in the analyzed roadside dust is much higher.

B. Assessment of pollution

Atmospheric particles mainly come from low-temperature crustal weathering, soil remobilization (crustal source), and a variety of anthropogenic sources at high temperatures. Enrichment factors (EF) are used to prove the chemical nature and principal sources of trace elements in aerosols by incorporating reference elements, and evaluate the strength of the crustal and non-crustal sources using Eq. (1), based on the

TABLE 1. Global comparison of heavy metal levels (µg/g) in roadside dust with Islamabad I-9 sector data

City/Country	Cd	Cu	Ni	Pb	Zn
AFRICA					
Luanda/Angola [1]	1.15	41.78	10.35	351.33	16.6
ASIA					
Amman/Jordan [16][36]	3.1-11.2	66.5-350	43-88	210-1131	166-410
Bahrain [5]	72–126	697.2	151.8	_	_
Beijing/China [17]	1.67	42	72	126	167
Calcutta/India [18]	3.12	44	42	536	159
Dhaka/Bangladesh [19]	_	46	26	74	154
Hong Kong/China [4]	2.18	24.8	_	93.4	168
Istanbul/Turkey [20]	1.5-2.3	49-234	30–33	105-556	447-594
Taejon/Korea [21]	_	47–57	_	52-60	172-214
Islamabad/Pakistan ^a	1.5	100.2	58.3	128.0	162.3
Islamabad/Pakistan					
reference value [15]	5.59	25	32	62.5	91
EUROPE					
Birmingham/UK [22]	1.62	466.9	41.1	48	534
Madrid/Spain [23]	_	188	44	1927	476
Oslo/Norway [23]	1.4	123	41	180	412
Palermo/Italy [24]	1.1	98	14	544	207
Paris/France [25]	1.7	1075	25	1450	840
Sweden [6]	0.32	79	12	53	220
NORTH AMERICA					
Hermosillo/Mexico [26]	4.25	26.34	4.7	36.15	387.98
Honolulu/Hawaii USA [27]	_	167	177	106	434
Ottawa/Canada [28]	0.37	65.84	15.2	39.05	112.5

a Present study

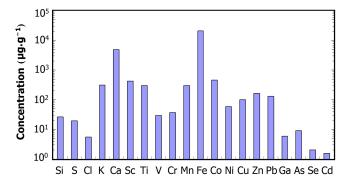


Fig. 1. (Color online) Mean concentration of elements in the road-side dust of Islamabad.

Earth's crustal mean abundance of the metals given by Wedepohl in 1995 [29], which are indicators of a specific source. Ti is used as a crustal indicator element.

$$EF_x = (C_{xp}/C_{Tip})/(C_{xc}/C_{Tic}), \tag{1}$$

where EF_x is the enrichment factor for element x, C_{xp} and C_{Tip} are the concentrations of x and Ti in aerosol, respectively, and C_{xc} and C_{Tic} are their concentrations in an average crustal material.

When EF_x approaches unity, crustal soils become the predominant source for element x. The EF values of trace elements in sources are expected to be greater than 1.0, save for

crustal materials. However, since crustal material types and soils originate from different areas, and little is known about uncertainties of fractionation during weathering, the EF values are better resolvable within 10 or a little larger for crustal materials (Fig. 3). The EF of elements, such as Cl, V, Mn, Fe, Ca, and K are close to unity or less than 10, suggesting that they are attributable mainly to crustal sources. The high enrichment values for Cr, Cu, Pb, Zn, As, Se, Cd, Ni, Co and S suggest that their dominant sources are non-crustal and various pollutant emissions may contribute to their loading. Higher EF values of elements show heavy metal contamination level in the roadside dust. This enrichment analysis confirms that the trace elements come from a mixture of crustal particles and anthropogenic sources in the roadside dust of Islamabad. The EF values of Cu, Pb and Ni were 60.22, 84.2and 22.4, respectively.

Copper is an essential trace element which is widely distributed in the environment and it occurs naturally in elemental form and as a component of many minerals. It is present in flora and fauna, and in various foods and beverages, including drinking water. Severe inhalation exposure to Cu dust or fumes at concentrations of $0.075-0.12\,\mathrm{mg/m^3}$ may cause metal fume fever with symptoms such as cough, chills and muscle ache [30]. The recommended safe and adequate dietary intake for Cu is $1.5-3.0\,\mathrm{mg}$ per day for adults, $0.7-2.5\,\mathrm{mg}$ per day for children and adolescents, and $0.4-0.7\,\mathrm{mg}$ per day for infants [30]. The findings of this study regarding copper were: The average concentration of Cu in the roadside dust samples from Islamabad I-9 sector, as given in Table. 1,

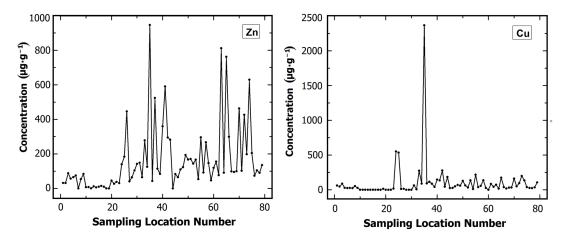


Fig. 2. Concentration of Zn and Cu in roadside dust samples collected at different locations in sector I-9 in Islamabad.

is $100.2\,\mu\text{g/g}$. This value is greater than $25\,\mu\text{g/g}$, which is the Cu average concentration in the soil. The variation in Cu concentration with sampling location observed in this study is shown in Fig. 2. The global concentration of Cu as reported in Table 1 varies from $25\,\mu\text{g/g}$ to $1075\,\mu\text{g/g}$. From the 19 places in Table 1, 8 places have higher and 11 places have lower Cu concentrations than that found in Islamabad.

Nickel is found in the earth's crust in combination with other elements. It is present in all soils, and in the environment where it is in combination with oxygen or sulfur as oxides or sulfides. Nickel is also released into the atmosphere through burning coal and oil in power generator plants. Health hazards from Ni exposure in the occupational environment are due primarily from inhalation. About 10% of women and 2% of men in the world are extremely sensitive to Ni exposure. The most common type of reaction to Ni exposure is skin rash called nickel dermatitis through direct contact with Ni [31]. The following results were obtained in the present study. The concentration of Ni as given in Table. 1 is 58.3 µg/g. In the soil samples, the average concentration of Ni was found to be 32 µg/g. The highest Ni concentration, 347.6 µg/g, was found in sample No.55. From these results it would appear that there is a higher Ni contribution from sediments and soils in roadside dust and also from traffic emissions. The amount of Ni measured at all sampling points along Islamabad I-9 sector was two times higher than the reference value [15]. The concentration of Ni measured at various places around the world is given in Table 1, and it varies from 4.2 µg/g to 177 µg/g. In Table 1, there are 4 places where the level of Ni is greater and 13 places where it is lower than that found in Islamabad.

Zinc is an essential trace element which is present in soil. It can cause deficiency symptoms and can be toxic when intake and exposures exceed physiological needs. The primary source of Zn exposure to people is from food, though oral exposure can become excessive through non-dietary sources. Certain occupational exposures can be hazardous. High Zn levels may disrupt the homeostasis of other essential elements. The observations made from Zn results in this study were as follows: In Table. 1 it can be seen that the average Zn

concentration found in roadside dust samples was $162.6\,\mu\text{g/g}$, and this is higher than the average Zn concentration ($91\,\mu\text{g/g}$) in soil. The global concentration of Zn in Table 1 is in the range $16.6-840\,\mu\text{g/g}$. In Table 1, there are 13 places where the Zn concentration is greater and 5 places where it is lower than the $162\,\mu\text{g/g}$ found in the roadside dust of Islamabad.

Lead is ubiquitous in industrialized societies, and evidence of the negative effects of Pb on humans has been noted for centuries. Lead poses a unique threat to developing minds and learning capacities of young children, who can be exposed from eating Pb-based paint chips or playing in contaminated soils. Pb can also damage the nervous system, kidneys, and reproductive system. The observations made from Pb results in this study were as follows: From Table 1, it can be seen that the average Pb concentration was 128 µg/g in the roadside dust samples and 62.5 µg/g in the soil samples. The highest Pb concentration in the dust samples was about twice the average Pb concentration found in the soil [15]. The high Pb concentration could have been due to traffic burden, brick kilns, and usage of leaded gasoline, which was phased out in Pakistan in 2005. Furthermore, most of the light vehicles on this highway use CNG (compressed natural gas), therefore the concentration of Pb is somewhat under control and should decrease with the passage of time. From the compiled data given in Table 1, it is evident that there is a big variation in Pb concentration from city to city; the concentration varies from 11.2 µg/g to 1927 µg/g. There are 7 places where Pb concentration is greater, 10 places where concentration is lower and one place (Beijing China) where the concentration is comparable to that in the dust of Islamabad industrial area.

C. Correlation of metal levels in roadside dust samples

In order to establish inter-elemental relationships in the roadside dust samples, principal component analysis was applied to the whole elemental concentration data set. Principal component analysis is an important method for qualitative source distribution in the study of aerosols [32]. Its purpose is to establish the minimum factors which can explain

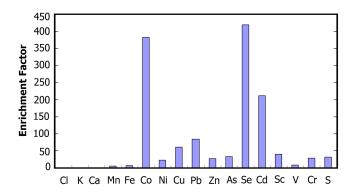


Fig. 3. (Color online) Enrichment factor of elements in roadside dust of Islamabad.

TABLE 2. Rotated component matrix of elemental mass concentration in roadside dust

Elements	Factor 1	Factor 2	Factor 3
S	0.080	0.036	0.761
Cl	0.379	-0.203	0.690
K	-0.036	-0.054	0.757
Ca	0.758	-0.389	0.200
Sc	0.702	0.657	0.178
Ti	0.638	-0.058	-0.050
V	0.731	-0.324	0.624
Cr	-0.342	0.842	0.030
Mn	0.726	-0.424	0.084
Fe	0.827	-0.433	0.128
Co	0.522	0.821	-0.020
Ni	-0.080	0.795	-0.347
Cu	0.279	0.586	-0.514
Pb	0.329	0.891	-0.431
Zn	0.306	0.740	-0.583
Ga	0.373	0.896	-0.069
As	0.468	-0.161	0.498
Se	0.022	0.245	0.634

the main variance of the system. Statistical analysis software SSPS10.0 was used for rotated component matrix factor analysis of element mass concentration in the dust samples (Table 2). The first, second and third factors are 80.8, 10.2 and

1.5%, respectively. It is sufficient to retain the three factors to explain 92.5% of the total variance. The first factor has high loading for Ca, Sc, Ti, V, Mn and Fe suggesting that these elements come from geological resources [33]. The second factor is related to Cr, Cu, Ni, Pb, Zn and Ga, indicating an industrial or traffic source, probably comprising different sources from industrial emissions [15, 34], while the third factor shows high loading of S, Cl, K, As and Se, suggesting that they may have originated from oil/coal combustion [35].

IV. CONCLUSION

Road dust is an increasing problem for developed and developing countries and is a source of various diseases. Roadside dust samples collected in sector I-9 of Islamabad were investigated for the presence of Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Pb, Zn, Ga, As, Se and Cd using PIXE. The concentration levels of these elements were generally higher in comparison with what is currently available in the literature. The relationship between different elements showed that Co, Ni, Cu, Pb and Zn are the contaminants which may have originated from industrial pollution/vehicles. The numbers of industries and vehicles in sector I-9 of Islamabad have grown rapidly in the past few years. Due to rapid industrialization and urbanization of Islamabad, the population of sector I-9, in particular, and the whole of Islamabad, in general, is expected to be even more in the coming years. Some preventive measures like using public transport, converting liquid fossil fuels into gaseous form and setting up more green areas can be employed to arrest this problem. We recommend that besides periodic heavy metal monitoring in road dust on the highway, regular air sampling should be carried out so as to observe seasonal pollution patterns in this area.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Arshad Munir, Director General of Experimental Physics Department for guidance and support.

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